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Experimental Design for One Dimensional Electrolytic Reactive Barrier for Remediation of Munition Constituent in Groundwater

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Abstract

A combination of direct electrochemical reduction and in-situ alkaline hydrolysis has been proposed to decompose energetic contaminants such as 1,3,5-Trinitroperhydro- 1,3,5-triazine and 2,4,6-Trinitrotoluene (RDX) in deep aquifers. This process utilizes natural groundwater convection to carry hydroxide produced by an upstream cathode to remove the contaminant at the cathode as well as in the pore water downstream as it migrates toward the anode. Laboratory evaluation incorporated fundamental principles of column design coupled with reactive contaminant modeling including electrokinetics transport. Batch and horizontal sand-packed column experiments included both alkaline hydrolysis and electrochemical treatment to determine RDX decomposition reaction rate coefficients. The sand packed columns simulated flow through a contaminated aquifer with a seepage velocity of 30.5 cm/day. Techniques to monitor and record the transient electric potential, hydroxide transport and contaminant concentration within the column were developed. The average reaction rate coefficients for both the alkaline batch (0.0487 hr^{-1}) and sand column (0.0466 hr^{-1}) experiments estimated the distance between the cathode and anode required to decompose 0.5 mg/L RDX to the USEPA drinking water lifetime Health Advisory level of 0.002 mg/L to be 145 and 152 cm.

1. Introduction

Groundwater contaminated with munition constituents such as 1,3,5-Trinitroperhydro-1,3,5- triazine (RDX) and 2,4,6-Trinitrotoluene (TNT) are found near explosive manufacturing, load and pack munition assembly, and demilitarization of munition (demil) facilities. Traditional treatment technologies for deep aquifers includes pump and treated granular activated carbon (GAC) [1] and in-situ bioremediation by addition of electron donor amendments [2]. Technologies for decomposition of munition constituents at explosive manufacturing along with load and pack facilities include GAC [3,4], anaerobic fluidized bed reactors [5] and alkaline hydrolysis [6,7].

Alkaline hydrolysis decomposes RDX into small organic and inorganic molecules. The high pH attacks the functional groups of the energetic molecule. Energetic nitramines decompose to form nitrate, nitrites, ammonia, nitrogen, hydrogen, organic acids and formaldehyde. Mechanisms for alkaline decomposition of RDX in batch studies have been reported [6–9].

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The reduction of energetic compounds such as TNT, and RDX and their kinetic transformations in separate electrode compartments are discussed by [10–12]. The in-situ use of direct electrochemical (e^- -barrier) for the removal of RDX and TNT were studied in column studies by [13,14] by sequential anode and cathodes with an electric potential 5 to 10 volts under constant current of 10 and 20 mA. A field scale pilot demonstration of the e^- -barrier treatment concluded the installed electrode system would last over 10 years [15].

An alternative deep aquifer treatment concept (Fig. 1) using the combination of direct electrochemical reduction and in-situ alkaline hydrolysis was introduced [16,17]. Placing electrodes in a flowing aquifer will result in acid and base fronts to migrate with the groundwater flow. By placing the cathode (–) upstream of the anode (+), the alkaline front produced will migrate downstream by advective hydraulic flow and ion migration towards the anode. The resulting reducing zone initiates the decomposition of aqueous RDX. An electron added during reduction destabilizes the molecule resulting in decomposition to small organic and inorganic molecules. At the cathode, some of the nitrite (product of RDX decomposition) will be converted to ammonia and nitrogen gas, RDX ring cleavage products, formaldehyde and methylenedinitramine (MDNA), a short lived intermediate of RDX decomposition which spontaneously decomposes to formate and nitrite. The aqueous organic product of RDX decomposition formaldehyde decomposes as it migrates towards the anode in the alkaline front. Some of the remaining organics (methanol and formate) and inorganic nitrite will undergo oxidation at the anode producing carbon dioxide.

The objective of this research was to evaluate laboratory methodologies for assessing the performance of the process and develop design parameters for up-scaling to a larger system.

2. Experiments

This section describes the details of both batch and sand column experiments along with the equations used to model the parameters required to up-scale the treatment concept to a larger system.

2.1 Chemicals and solutions

RDX-stock solutions were prepared from solid RDX procured from Holston Ammunition Plant (Kingston, TN) in organic-free reagent grade water ($6\ \mu\text{S}/\text{cm}$, $\text{pH} = 6.8$) stirred for 48 hours. The stock solutions were diluted to target experimental solutions of 0.5 and 1.0, mg/L. The RDX and its known nitroso-transformation products (MNX, DNX, and TNX) aqueous phase concentrations were analyzed from batch reactors, the column influent and effluent streams, electrode wells, and the sampling ports along the column length with a modified EPA Method 8330 using a Dionex HPLC system (Sunnyvale, CA). When column effluents were below the 0.02 mg/L laboratory reporting limits, solid phase extraction cartridges (Waters Sep-Pak SPE) concentrated one day's effluent volume for RDX analysis. A Dionex 2500 ion chromatograph (IC) analyzed inorganic ions chloride, nitrate and nitrite along with organic acids such as formate that are the final end-products of RDX decomposition by alkaline hydrolysis and electrochemical reduction.

2.2 Batch Experiments

A series of batch experiments assessed alkaline hydrolysis and electrochemical decomposition of RDX. The RDX analytical results were modeled with a two-parameter nonlinear exponential decay equation to determine pseudo-first order reaction rate coefficients with respect to RDX concentration,

$$C = C_0 e^{-kt} \quad (1)$$

where C represents RDX concentration (MT^{-1}) at anytime, t (T) the initial concentration, C_0 (MT^{-1}) and k represents the first order kinetic coefficient (T^{-1}).

In order to limit human error associated with sample collection, an automated custom panel mounted timer/controller was assembled to simultaneously collect samples from the triplicate batch reactors. The sampling system operated three normally closed solenoid valves. Each sample collection cycle consisted of a global time, outlet purge, tray advance, sample collection, and another tray advance. The samples from each reactor vessel were collected by gravity through a solenoid valve into 20-mL amber glass vials resting on a fraction collector tray (Fig. 2).

Batch alkaline hydrolysis used 500 mL aspirator bottle (Corning No.: 1220) as batch reactors because they contained tubular sidearm outlet (10mm O.D.) near the bottom for sample extraction (Fig. 2). The experiments used RDX concentrations of 0.5 or 1.0 mg/L with hydroxide concentrations corresponding to pH levels 11, 11.5, 12, and 12.5. Samples from these triplicate experiments poured from the reactors into the collection vials simultaneously in 3 mL aliquots at specific timing increments. The collection vials pre-spiked with an appropriate volume (50 to 100 μL) of 2 M hydrochloric acid quenched the alkaline hydrolysis reaction and preserved the sample below pH 3.0. To confirm that the hydroxide concentration remained constant throughout the experiments, a titration equation using the resulting acid pH readings along with the hydrochloric acid volumes added to the sample back calculated the initial hydroxide concentration.

2.4 Electrochemical Batch Experiments

The electrolytic batch experiments mimicked the alkaline hydrolysis experiments RDX concentration at neutral pH except that anode and cathode (5×1 cm) electrodes spaced 5-cm apart were inserted into the aspirator bottles. The dimensionally stable electrodes were of mixed metal oxide catalyst sintered to an expanded titanium mesh (ElgardTM 85 mesh, Corpro Companies, Inc., Medina, OH). An Agilent Model E3612A dc power supply (60–120V/.5–.25A Dual) operated in constant current mode supplied the electric power to each reactor bottle (Fig. 3). Triplicate experiments used current settings of 4, 10, and 20 mA.

2.5 Horizontal Sand Column Experiments

The horizontal sand columns were constructed of clear polyvinyl chloride (PVC) column (70.5 cm long by 5 cm ID) containing one anode and cathode [16]. The columns filled with washed sand (20×40 Oglebay Norton Industrial Sand, Brady Texas) had an effective grain size (D_{10}) of 0.5, a uniformity coefficient of 1.24, and a hydraulic conductivity of 0.11 ± 5.3 (10^{-3}) cm/s. The column construction consisted of pipe tees, short pipe sections, and flanges. The inlet and outlet flanges included porous polyethylene filter material confining the sand in the column. Cathodes and anodes were installed in #10 slotted PVC (0.254 mm openings) well screens (1.25 cm ID) spaced 35 cm apart. The electrodes were of the same material and dimensions as those used in the electrochemical batch experiments (Fig. 4). Two Sorensen 300V–3A power supplies connected in series provided 600 volts maximum output and operated in constant current mode set to 20 mA. Influent water with either 0.5 mg/L or 1 mg/L RDX was pumped through each column by a FMI RH (Syosset, NY) piston pump head attached to a Cole Parmer drive motor (model 7550–20).

Because the electric potential distorts direct pH electrode readings, four sets of ports between the cathode and anode wells were installed to circulate the fluid across each column

at the same horizontal distance from the cathode. The four pairs of ports were installed at 4, 10, 21, and 28 cm from the cathode with the port label numbers increasing from the cathode. Fluid from the outlet ports circulated from the front to back of each column by an Ismatec IP (Glattbrugg, Switzerland) multi-channel peristaltic pump with 0.64 mm ID PVC pump tubing. A cross circulation flow of 0.05 mL/min with a hydraulic retention time less than one hour per port supplied new fluid to each pH electrode (Sensorex S200CD) every 5 minutes (Fig. 5). A paperless chart recorder (Fuji Electric PHL21B11-E10Y, Pathfinder Instrument, Carlsbad, CA) collected the pH data from the JENCO Model 692 pH transmitters. Fluid from the column ports and effluent were analyzed for RDX concentrations at specific time intervals.

Prior to electrode well installation, non-reactive chloride tracer (breakthrough) tests with and without cross circulation determined the hydrodynamic properties of each column, particularly dispersivity and porosity. An Eldex Universal Fraction Collector (UFC) received the effluent samples in 40 mL vials at specific time intervals. Tracer tests results from the IC were modeled with an analytical solution for one-dimensional advective-dispersive solute non-reactive transport equation, [19] to determine the effective porosity and dispersivity. The analytical solution by [19] is

$$C = \left(\frac{C_0}{2} \right) \left[\operatorname{erfc} \left(\frac{x - vt}{2 \sqrt{\alpha v t}} \right) + \exp \left(\frac{x}{\alpha} \right) \operatorname{erfc} \left(\frac{x + vt}{2 \sqrt{\alpha v t}} \right) \right] \quad (2)$$

where C and C_0 are the fitted and initial solute concentrations (M L^{-1}) and α the dispersivity coefficient (cm), x specific distance along the column from the inlet (L), v the seepage velocity (LT^{-1}) and t (T). The solved parameters were used to adjust the influent pumping rate for each column to match the target seepage velocity of 30.5 cm/day.

Because alkaline hydrolysis by electrolysis experiments combine two decomposition processes, it was necessary to assess alkaline hydrolysis in separate experiments without electrolysis. For the alkaline column experiments sodium hydroxide solution $[\text{OH}^-]$ 31.6 mM (pH 12.5) was pumped into the cathode well at 40 mL/day while the influent RDX was either 0.5 or 1.0 mg/L. Samples (700 μL) extracted from each set of column ports were pipetted into sample vials containing 20 μL of 2 N HCl to preserved the samples for RDX analysis.

The reaction rate coefficients of RDX decomposition by alkaline hydrolysis in the sand columns was determined by an approximate analytical solution to the one-dimensional advective-dispersive first-order decay solute transport [19],

$$C = C_0 \exp \left[x \left(\frac{v - \sqrt{v^2 + 4k\alpha v}}{2\alpha v} \right) \right] \quad (3)$$

where C_0 is the constant inlet concentration (MV^{-1}), C is the concentration (MV^{-1}) at any distance x (L) from the inlet, α is the dispersivity (L) v is the seepage velocity (LT^{-1}) $v = q/(A \cdot n)$, n = porosity, and A is column cross sectional area (L^2) $x = vt$ and k is the pseudo first-order decay coefficient (T^{-1}). By substituting b into the interior parenthesis of the equation above

$$-b = \frac{v - \sqrt{v^2 + 4kv}}{2\alpha v}, \quad (4)$$

it becomes a first-order decay equation of the form, $y = a \exp(-bx)$ that can be solve for b (L^{-1}) at any distance x along the horizontal sand column by non-linear regression. Finally setting $k = bv(ab+1)$, the reaction rate coefficient in reciprocal length was converted to reciprocal time for use in (4).

3. Results and Discussion

The batch and the horizontal column experiments results provided kinetic coefficients and to adapt equations to predict the length of an up-scaled horizontal flow column. Because of the diversity of experiments, results and discussion of results for individual experiments are combined.

3.1 Alkaline and Electrochemical Batch studies

Hydrolysis of RDX shows first-order dependence with hydroxide concentration (Fig. 6a). The higher the hydroxide concentration placed in solution, the larger the reaction rate coefficient of RDX removal. The results indicate that alkaline hydrolysis of RDX is not practical below hydroxide concentrations of 3.16 mM (pH 11.5). The reaction rate coefficients hydroxide concentrations corresponding with pH 11.5 and 12 are similar to [18] but the rate coefficients at lower and higher concentrations differ. A practical hydroxide concentration for the column experiments appears to be 10 mM (pH 12) or above, with a 4 to 5.6 hour half-life allowing decomposition to occur within the 56 hour column hydraulic retention time.

For the electrochemical batch experiments, higher electric current input produces larger reaction rate coefficients (Table 1 and Fig. 6b). Additional batch titrations were conducted with current settings of 6, and 8 mA without replication to fill between the 4 and 10 mA triplicate kinetic data. The results of the batch electrolytic hydrolysis studies are consistent with those reported in the literature [10,12] that increased the electric current results in larger the reaction rate coefficients. It was determined that 20 mA of applied current should be used for the sand filled column experiments because it will produce a 3.2 mM hydroxide concentration [16,18]. The 20 mA current also produced a target pH of 12.5 that was similar to the kinetic coefficient determined from the alkaline hydrolysis batch experiments (Table 1).

3.2 Alkaline hydrolysis under flow (without electrolysis)

Three horizontal sand column experiments with RDX influent concentrations of 0.5 and 1.0 mg/L determine the reaction rate coefficients of RDX decomposition by alkaline hydrolysis by pumping sodium hydroxide into the cathode well without electric current (no electrolysis). The chloride tracer tests with and without cross-recirculation (for pH measurement) determined the effects on the dispersivity and porosity calculations. The average dispersivity results in the three columns with and without cross circulation were 0.140 ± 0.036 and 0.140 ± 0.026 cm (Table 2).

After hydroxide injection, the column flow and pH were allowed to stabilize for seven days before sampling. Samples taken from each port in 4 or 5 day intervals for RDX analysis insured column conditions were as close to steady-state as possible. The average pH for all ports, sample times, and columns was 12.1 ± 0.3 . The pH in Column C at each sample beginning at the cathode well and ending with the anode well shows an initial drop in hydroxide concentration in Port 1 followed by stable above pH 12 (Port 2 and 3) and

diminishing to pH 11.9 in Port 4 and the anode well (Fig. 7). The consistent lower pH in Port 1 can be attributed to the advective dominated flow and incomplete mixing 4-cm following the hydroxide injection.

Individual and average reaction rate coefficients results by column for the 0.5 and 1.0 mg/L RDX inlet concentrations are elucidated in Table 3. An overall rate coefficient for the 0.5 and 1.0 mg/L RDX influent were 0.053 ± 0.014 and $0.059 \pm 0.015 \text{ h}^{-1}$. The first order fitting parameter, b , for the combined 0.5 and the 1.0 mg/L experiments with the standard deviations are shown in Fig. 8a, b. The reaction rate coefficients were similar the batch pH 11.5 experiments. Since there was limited chemical contact and incomplete mixing in the sand pore spaces lower rate coefficients are expected when compared with liquid only batch experiments.

3.3 Alkaline Hydrolysis Generated by Electrolysis Column Experiments

These experiments evaluated electrolytic generated alkaline hydrolysis for transformation of RDX concentrations (0.5 mg/L) in horizontal sand columns Prior to the installation of the electrode wells, chloride tracer tests results using the non-reactive transport model determined the average dispersivity and porosity of the three columns to be 0.200 ± 0.061 and 0.383 ± 0.006 (Table 4).

3.3.1 Hydroxide transport—After the effluent RDX equaled the influent concentration, power to the electrodes was applied. Data recorded in 30-minute intervals for the initial 24 hours (10 d) provided knowledge of the hydroxide front development and migration through each column by sample port. The initial hydroxide data in terms of pH for all three columns were similar for the first 240 hours of treatment with Column C illustrated in Fig. 9a, b). Within five hours after the electrodes were energized, the pH in Ports 1 and 2 for all columns increased to greater than pH 11 with Columns B and C Ports 1 and 2 reaching a pH of 11 in less than 3 hours (Fig. 9a). In all columns, the pH in Ports 1 and 2 continued to increase to greater than pH 12 where it remained steady for the remainder of each experiment. The pH in Port 4 for all three columns was affected by acid migration from the anode toward the cathode causing the pH to oscillate from 4.5 to 11 until the alkaline front overwhelmed the acid front near these ports. Based the seepage velocity and port distances from the cathode being 4, 10, 21, and 28 cm for Ports 1 through 4, it should take 7.8, 6.1 and 7.1 hours (Columns A, B and C), for the hydroxide to reach Port 2 of each column. For Port 2, the hydroxide transport was 2.6, 2.0, and 2.4 times faster than the seepage velocity. By flow alone it should take 17, 16.5 and 16.7 hours (Column A, B, C) for the hydroxide to reach Port 3. However for Port 3 hydroxide transported 3.6, 5.0, and 6.2 times faster than by flow, reflecting an effective migration rate of 107.2, 152.7, and 186.7 cm/day for the three columns averaging $148.9 \pm 32.6 \text{ cm/day}$. At the same time, the proton produced at the anode migrated towards the cathode, retarding the hydroxyl front transport to Port 4. After 36 hours of treatment the hydroxide front overwhelmed the acid front at Port 4 upstream of the anode where the pH remained greater than 11.5 throughout the remainder of the experiments. The effluent pH for all columns decreased from 7 to less than 4 in less than 5 days of treatment with occasional oscillations from neutral to alkaline pH with the exception of Column A (Fig. 10b)

3.3.2 Electric Potential—The initial electric potential was 600 V in each column but decreased to 160 V or less after 44 days with the constant current set tot 20 mA (9.9 A/m^2) throughout the experiment. Column A was terminated after 44 days while Column B and C experiments ran for 82 days with final voltages of 87 and 100 V, respectively. The initial and final voltage gradients for Columns B and C were 18.3 and 3 V/cm. As the column fluid became more ionized (conductivity increased), the electric potentials decreased and

remained relatively stable for the remainder of the experiment (Fig. 10c). The duration of each column test along other operational parameters are listed in Table #.

3.3.3 RDX analysis—The initial influent RDX concentration was approximately 0.5 mg/L for each column (Fig. 10a). The effluent RDX concentration decreased immediately after the electrodes were energized. The average effluent results for three columns after 23 days of treatment were 0.007 ± 0.004 , 0.030 ± 0.013 , and 0.036 ± 0.013 mg/L (Fig. 10a). The RDX removal percentages for these columns (A, B, and C) were 98.7, 94.3, and 93.2, respectively, with an average overall removal percentage of 95.4 ± 1.4 . RDX nitroso transformation products (MNX, DNX, and TNX) were not detected in the effluent.

3.3.4 Alkaline Hydrolysis by Electrolysis flow barrier RDX Results Summary—In the electrolytic alkaline hydrolysis reactive barriers, an initial influent RDX concentration of approximately 0.5 mg/L was used for each column (Fig. 10a). The effluent RDX concentration decreased to 0.07 mg/L in less than 4 days after the electrodes were energized. The effluent RDX concentrations were analyzed by solid phase extraction (SPE), after 18 days of treatment. The average effluent results for three columns after 23 days of treatment were 0.007 ± 0.004 , 0.030 ± 0.013 , and 0.036 ± 0.013 mg/L. The RDX removal percentages for Columns A, B, and C were 98.7, 94.3, and 93.2, with an average overall removal percentage of 95.4 ± 1.4 . RDX nitroso transformation products (MNX, DNX, and TNX) were not detected in the effluent. These results demonstrate that approximately 96 % of influent RDX concentrations (0.5 mg/L) were transformed under average electric current density of 9.9 A/m^2 in a porous media flow-through scheme.

4.1 Up-Scaling Calculations

The reaction rate coefficients from the alkaline column studies and the alkaline batch studies were used to calculate a required column length to decompose RDX between the cathode and anode. The column length calculations were from a rearranged (4) solved for x (cm). The constants used in the equation were an average dispersion coefficient, 0.14 cm, a seepage velocity, 30.5 cm/day, inlet and outlet RDX concentrations, 0.5 mg/L and 0.002 mg/L. The variables were the reaction rate coefficients in terms of (day^{-1}). The average rate coefficient for the individual sample events were 0.051 ± 0.014 and $0.049 \pm 0.015 \text{ h}^{-1}$ for the 0.5 and 1.0 mg/L inlet concentrations and combined sample event data rate coefficients were 0.0466 and 0.0491 h^{-1} . The average column length calculated from the individual samples for the 0.5 and 1.0 mg/L influent concentrations were 139 ± 32.7 and 141 ± 40.2 cm. With all of the individual samples combined the calculated column lengths were 138 and 144 cm from the two influent concentrations (Table 6).

4. Conclusions

An experimental design is developed for one dimensional electrolytic reactive barrier for remediation of munition constituent in groundwater. The design includes experimental setup and analytical approach for assessment and optimization. This design is used to evaluate alkaline hydrolysis generated from a cathode electrode under the flow of 30.5 cm/day seepage velocity in horizontal sand columns. Batch experiments show that hydroxide concentrations greater than 0.0316 M were required for the column studies and that RDX can be effectively decomposed in a mix electrode compartment system at rates similar to those reported for separate electrode compartment results [10,11]. A current density on the order of 9.9 A/m^2 at the cathode produced hydroxide concentrations sufficient to decompose $95.4 \pm 1.4\%$ of the influent RDX (0.5 mg/L) in horizontal sand column flowing under 30.5 cm/day seepage velocity. A semi-analytical one dimensional solution for advective-dispersive first-order decay solute transport model predicted that a distance of 150 cm

between cathode and anode electrodes is required to decompose RDX from an influent concentration of 0.5 mg/L to below the EPA Drinking Advisory Limit of 0.002 mg/L using reaction rate coefficients developed for these experiments.

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Fig. 1. Schematic of electrochemical barrier: (a) in situ application of a direct current across a cathode and anode; (b) placement of the cathode upstream (groundwater flow) of the anode; (c) RDX destruction by direct electrolysis; (d) destruction RDX by alkaline hydrolysis migrating toward the anode; followed by (e) oxidation at the anode.

Fig. 2.
Automated batch reactor sampling system

Fig. 3.
Electrochemical reactor used with the automated batch reactor sampling system

Fig. 4.
Horizontal sand column design for both alkaline hydrolysis under flow and alkaline hydrolysis under electrolysis

column cross section

Fig. 5.

Horizontal column cross circulation system designed to capture pH with time.

Fig. 6.
RDX decomposition vs Time (a) Batch alkaline hydrolysis and (b) electrochemical

Fig. 7. Alkaline hydrolysis under flow pH vs distance from inlet from the 1.0 mg/L RDX influent, Column C. Each data point along the column represents the cathode well, Ports 1 – 4, followed by the anode well

Fig. 8. Combined first order decay fit (cm), from alkaline hydrolysis column experiments by distance (a) 1 mg/L influent RDX (b) 0.5 mg/L influent RDX

Fig. 9. Alkaline hydrolysis by electrolysis Column C (a) Port pH vs time initial 24 hours of treatment (b) Port pH vs time initial 240 hours of treatment. Vertical lines represent the required time for pH 11 to reach Port 2 and Port 3 by flow alone. (Ports numbers increase from cathode to anode)

Fig. 10. Alkaline hydrolysis by electrolysis results vs. time (a) RDX (mg/L) (b) influent and effluent pH, (c) electric potential (V)

Table 1

Alkaline Hydrolysis and Electrochemical batch RDX reaction rate coefficients

pH	Alkaline Hydrolysis		Electrochemical	
	[OH ⁻] (mM)	k (h ⁻¹) × 10 ⁻³	Current (A) × 10 ⁻³	Current density A/m ²
11.0	1.0	8.3	4	1.55
11.2	1.6	26.9	6	2.32
11.5	3.2	67.9	8	3.1
12.0	10.0	125	10	3.87
12.5	31.6	309	20	7.74
				590

Table 2

Alkaline hydrolysis column under flow RDX decomposition rate coefficients

C_0 RDX (mg/L)	Parameter	$b \times 10^3$ (cm ⁻¹)	$k \times 10^3$ (h ⁻¹)	$t_{1/2}$ (h)
Column				
0.5	A	32.2	48	14.5
	B	46.6	68.8	10.1
	C	28.5	42.1	16.5
	Average ABC	35.8 ± 9.6	53 ± 14	13.7 ± 3.3
1.0	A	45.9	68.5	10.1
	B	45.3	66.9	10.4
	C	28.7	42.38	16.4
	Average ABC	40 ± 9.8	59.3 ± 14.6	12.3 ± 3.6

Table 3
Alkaline hydrolysis column under flow column parameters with and without cross-circulation

Column	A		B		C	
	No	Yes	No	Yes	No	Yes
Parameter						
Dispersivity, (cm)	0.116	0.102	0.139	0.173	0.167	0.143
Porosity, n	0.391	0.407	0.391	0.409	0.402	0.41
Flow, Q (mL/h)	10.56	11.23	10.28	10.84	10.67	10.51
Empty Volume (mL)	1403	1403	1425	1425	13834	1384
Pore Area (cm ²)	7.93	8.25	7.92	8.29	8.15	8.31
Pore Volume (mL)	549	571	557	583	556	567
Seepage Velocity, v (cm/day)	32	32.7	31.1	31.4	31.4	30.3
HRT(h)	51.9	50.9	54.2	53.8	52.1	54

Table 4

Alkaline hydrolysis by electrolysis column parameters

Parameters	column studies		
	Influent - 0.5 mg/L RDX		
	A	B	C
dispersivity (α) (cm)	0.17	0.27	0.16
porosity (n)	0.38	0.39	0.38
flow (Q mL/hr)	9.5 ± 0.3	9.6 ± 0.3	9.5 ± 0.3
seepage velocity (cm/day)	29.7 ± 0.9	30.5 ± 0.9	30.2 ± 0.82
empty volume (mL)	1412	1424	1424
pore area (cm ²)	7.5	7.9	7.7
pore volume (mL)	520	552	538
HRT (h)	52	51	51

Table 5

Operating Parameters for Alkaline Hydrolysis by electrolysis column flow experiments

Experiment		Influent - 0.5 mg/L		
Parameters	Columns	A	B	C
duration (d)		44	82	82
current (mA)		20	20	20
current density (A/m ²)		9.9	9.9	9.9
electrode surface area (cm ²)		16.3	16.3	16.3
electric potential	initial	605	605	603
(V)	final	162	87	100
voltage gradient	initial	18.3	18.3	18.3
(V/cm)	final	4.9	2.6	3

Table 6

Comparison of up-scale column length prediction by study

Treatment Process	Influent RDX (mg/L)	rate coefficient (10^{-3} h^{-1})	Half-life (h)	Predicted treatment length (m)
Alkaline Batch pH 11.5	1.0	48.7	14.2	145
Alkaline Hydrolysis under flow columns	0.5	51.1	13.6	138
	1.0	48.9	14.2	144